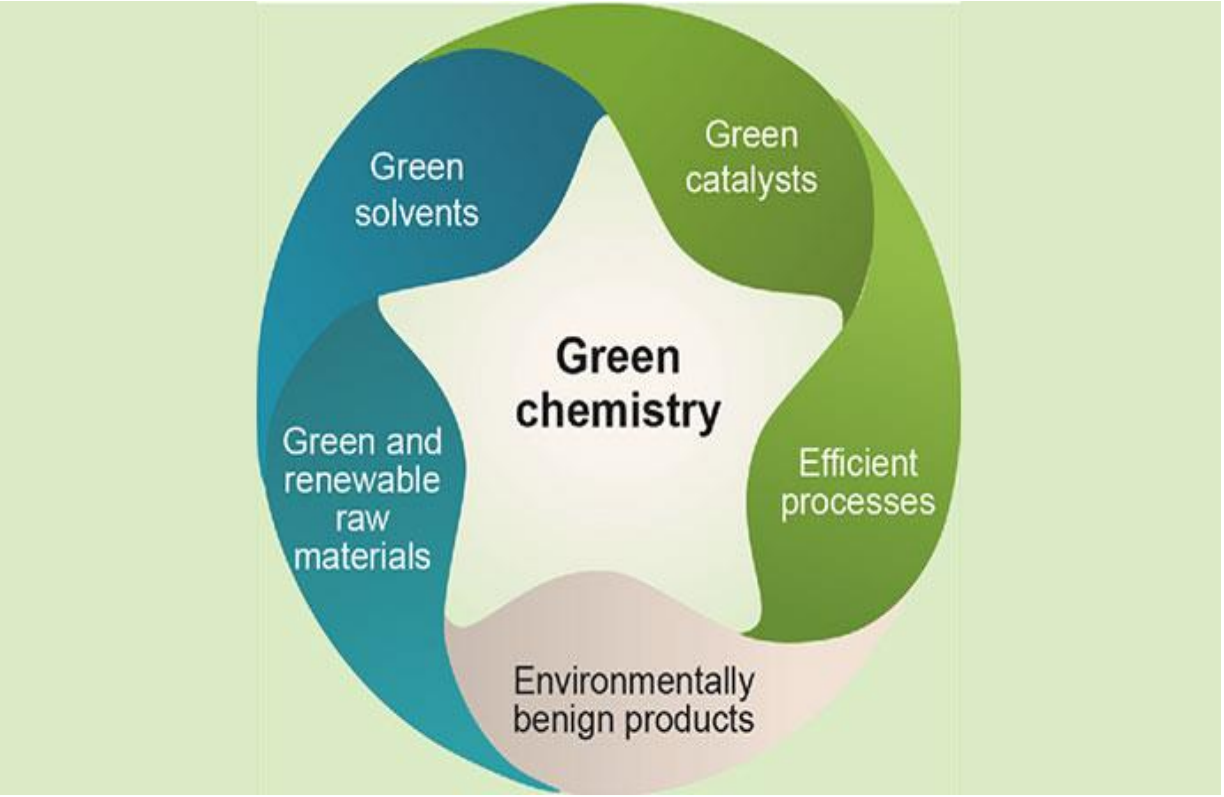
Investigation of Microwave Assisted Hydrogenations Using Frustrated Lewis Pairs

MoJo™

Green Chemistry

- Approach of chemical methods
- Reduce usage of hazardous substances
- Twelve principles of green chemistry



Twelve Principles of Green Chemistry

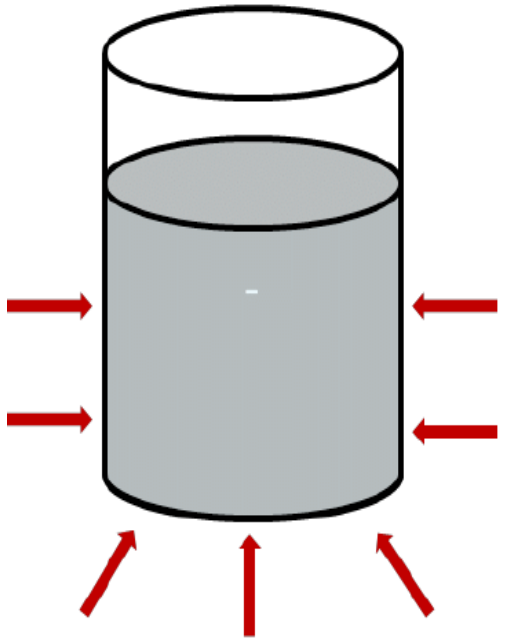
1. Prevent waste
2. Maximize atom economy
3. Design less hazardous chemical syntheses
4. Design safer chemicals and products
5. Use safer solvents and reaction conditions
6. Increase energy efficiency
5. Use renewable feedstocks
6. Avoid chemical derivatives
7. Use catalysts, not stoichiometric reagents
8. Design chemicals and products to degrade after use
9. Analyze in real time to prevent pollution
10. Minimize the potential for accidents

Twelve Principles of Green Chemistry

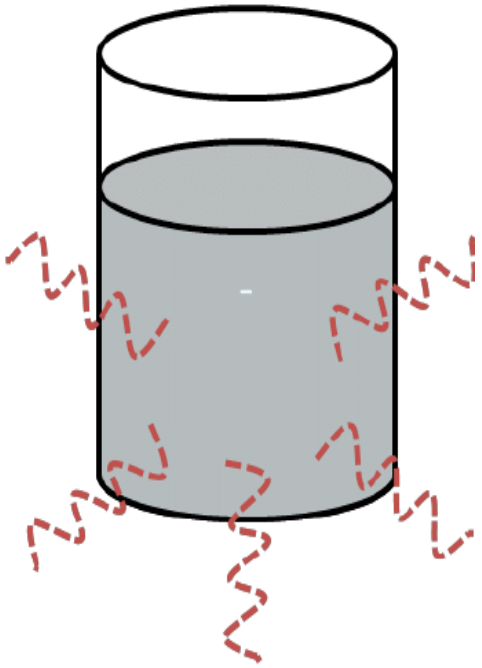
- Primarily focuses on quality control, safety control, safer solvents, energy efficiency and catalysis
- Used microwave irradiation instead of conventional heating

Microwave irradiation vs. conventional heating

- Conventional heating:
  - Inefficient
  - Time-consuming
- Microwave Irradiation
  - Electromagnetic energy converted into thermal energy
  - Molecules rotate, creating kinetic energy



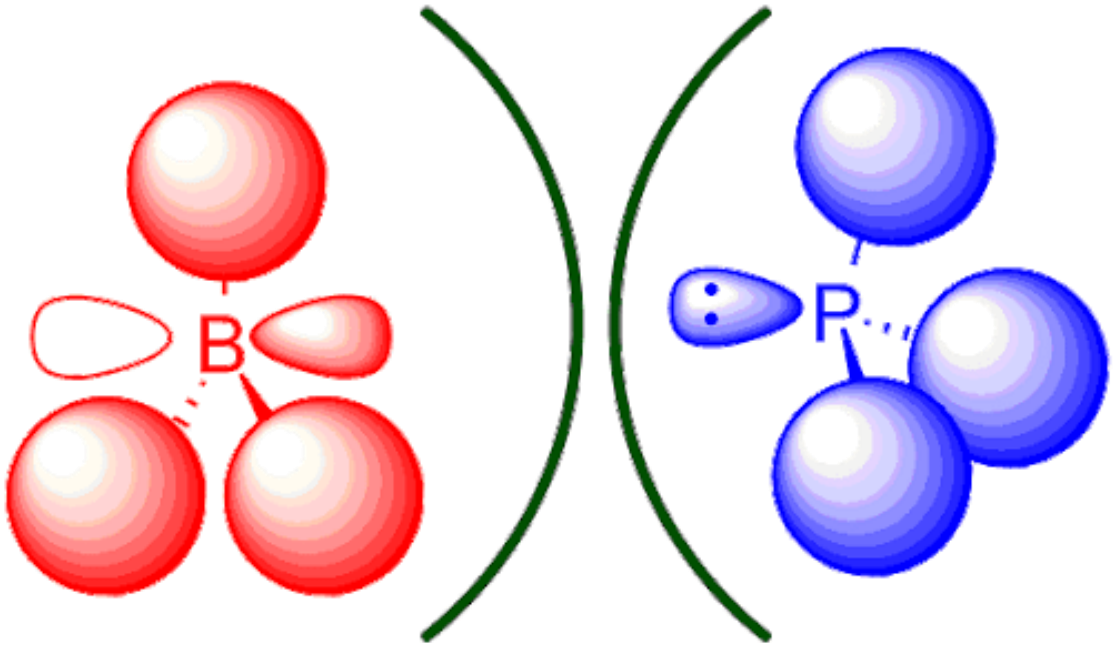
Conventional heating



Microwave heating

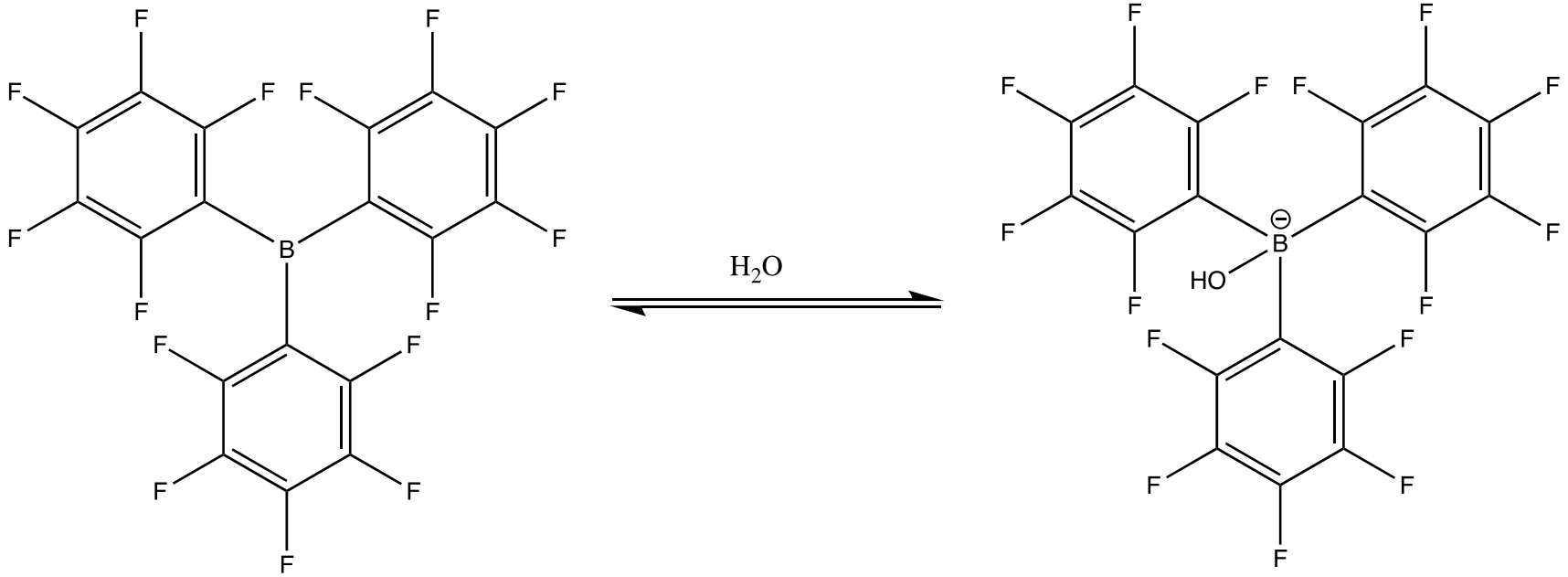
Frustrated Lewis Pairs

- Lewis acid and base pairs which cannot form adduct
  - Due to steric hindrance
  - Electrons are not able to be transferred from the base to the acid



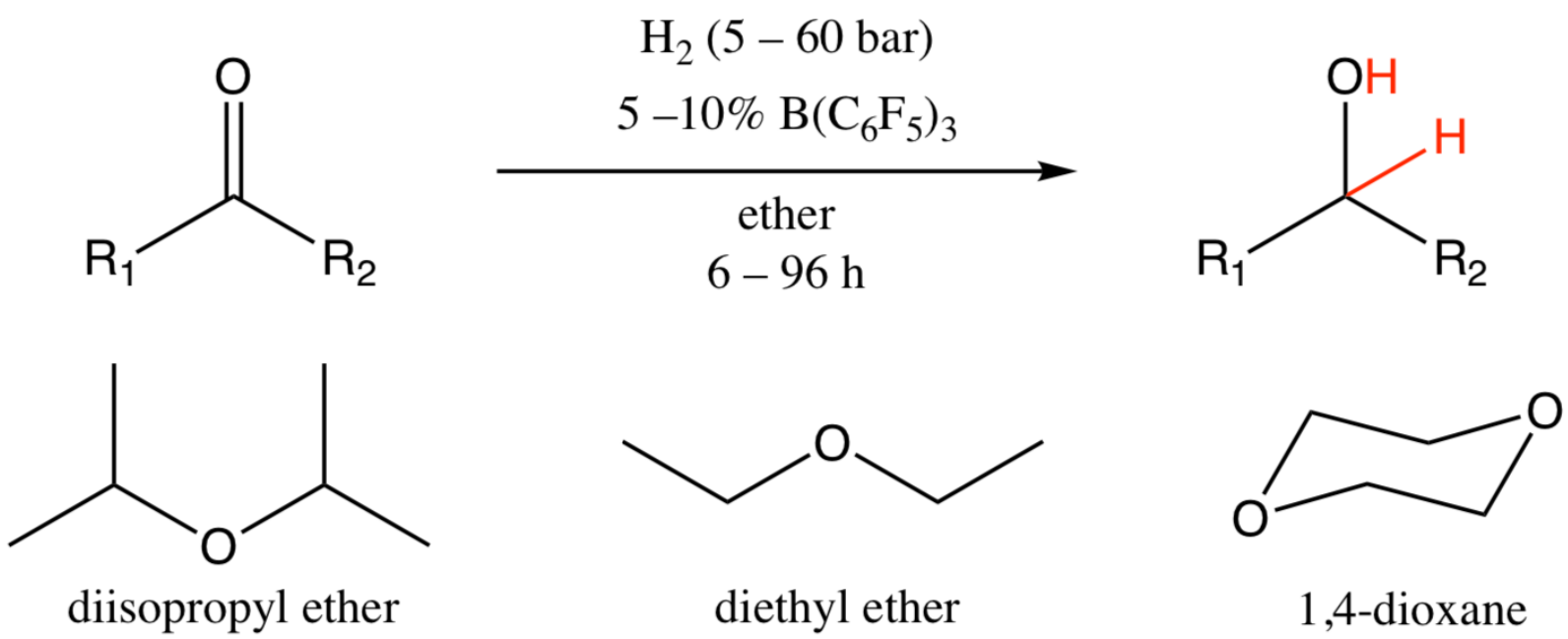
Using BCF as FLP Lewis Acid

- Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$
- Strong Lewis Acid
- Highly reactive with water



Limitations of Carbonyl reduction by FLPs

- Ethers are a safety and health hazard
- Has long reaction times at high temperatures
- Need high pressure & temperature for moisture
- BCF is air & moisture sensitive
  - Handled in glove box to stop quenching



diisopropyl ether

diethyl ether

1,4-dioxane

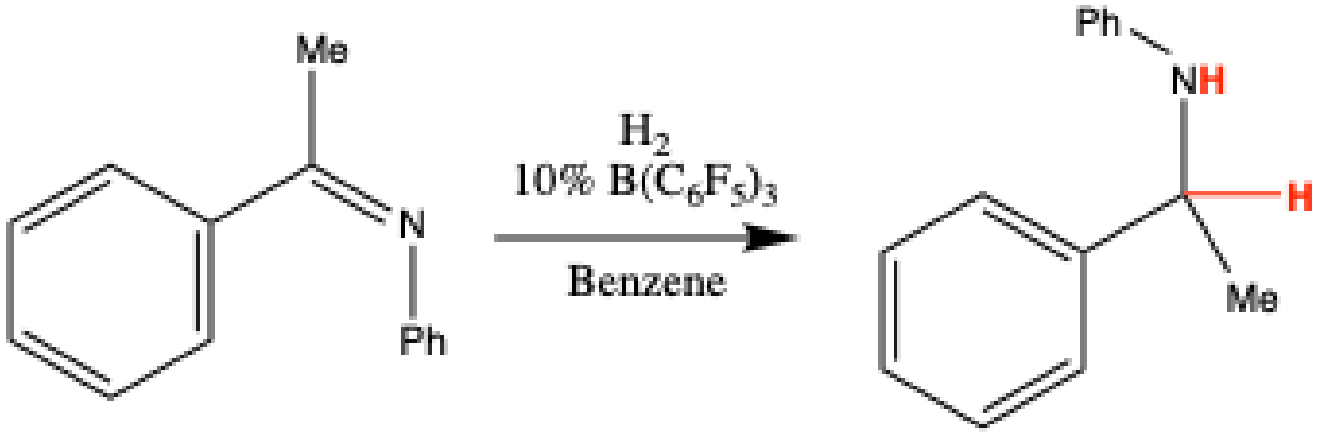
Dalton Trans., **2016**, 45, 6124

Goals

- To develop an easy, user-friendly method for FLP hydrogenations
- Shorten reaction time
- Use "greener" alternatives to minimize waste
- Using microwave as heating source

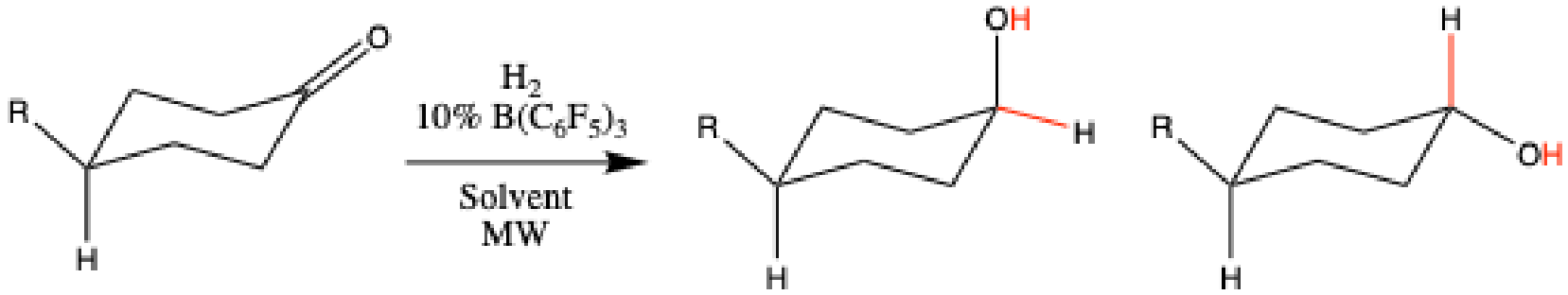
Microwave Example

- Benzene as solvent
- Not moisture tolerant (done in glove box)
- No carbonyl examples



Heating	Time	Yield
microwave	40 min	99
conventional	40 min	44
conventional	22 hrs	68

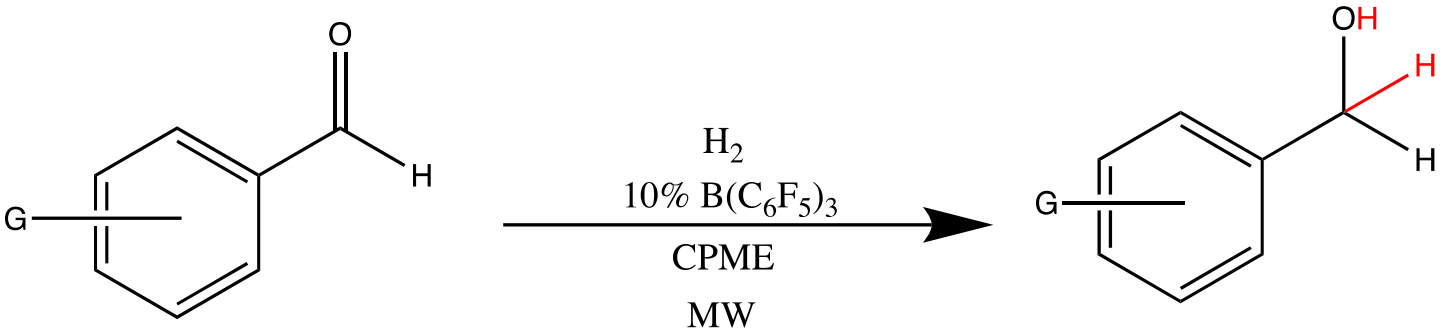
Hydrogenation of Cyclohexanones



Equitorial Attack Axial Attack

	Microwave Conditions			Conventional Conditions	
R	Solvent	% conversion	Time (h)	% yield	Time (h)
H	1,4-dioxane	85	3	58-92	12-39
	CPME	100	2.5	--	--
T-Bu	1,4-dioxane	100 (95:5)	2.5	98	88
	CPME	100 (95:5)	2	--	--
Me	CPME	99 (58:42)	0.75	--	--
2-Me	CPME	No reaction	> 2	--	--

Reaction Rates



- Varies G group
- First order reaction rates
- Moderate correlation between G and E_a

G	k_{110} (s^{-1})	R^2	E_a ($kJmol^{-1}$)
4-NO_2	3.64 x 10^{-4}	0.975	46
3-NO_2	3.06 x 10^{-4}	0.995	13
2-NO_2	3.06 x 10^{-4}	0.949	32
4-Cl	1.52 x 10^{-4}	0.951	66

Conclusions

- Microwave irradiation used successfully for FLP hydrogenations of carbonyls
- CPME was found to be a more benign and efficient solvent
- Reaction times reduced from days to minutes
- Reactions are monitored in real time
- Reaction rates (10^{-4} s^{-1}) were calculated
- Comparisons to conventional methods and mechanistic studies in the future